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EVALUATION OF COATINGS TO CONTROL ZEBRA MUSSEL COLONIZATION - YEAR ONE - INTERIM REPORT

Report 91-56-K

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ABSTRACT

The purpose of this study is to identify coatings that would be effective in protecting submerged concrete and steel surfaces from zebra mussel fouling. In March 1990, test plates coated with a variety of antifouling paints, were immersed in the western forebay of Nanticoke TGS. The following coatings were evaluated in terms of their ability to resist zebra mussel fouling or provide easily cleaned surfaces: a biodegradable wax, copper powder/polyester, polyurethane, drag reducing epoxy/polyamine, teflon and three different silicone rubbers. These were compared to uncoated controls and a standard coal-tar epoxy paint.

By October, based on visual appearance, only two paints demonstrated any resistance to mussel attachment. With both of these silicone based paints, mussel coverage ranged from 0 to 20% and mussels which were attached could be easily dislodged. All other antifouling coatings, the uncoated controls and the coal-tar epoxy standard failed to prevent permanent mussel attachment (33% to 100% attachment) .

Although after seven months two silicone coatings were effective, further biological evaluation and testing of physical performance of these paints will be carried out before their use can be recommended.

job	file	date	report no.
32-121	837.3	April 25, 1991	91-56-K

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EXECUTIVE SUMMARY

Zebra mussels (Dreissena polymorpha) are a species of freshwater mollusc indigenous to Europe and Asia. Since their introduction into the Great Lakes in the late 1980's, serious fouling problems have been experienced by industries drawing untreated lake water from Lake Erie and Lake St. Clair. It is expected that these mussels will infest all other Great Lakes and most freshwater systems in North America within the next few years.

Presently, Ontario Hydro is chlorinating the intakes of low pressure water systems to prevent mussel settlement. However, this is probably a short-term control method and due to environmental concerns, other mitigation techniques must be developed.

The use of antifouling coatings is a well known method of controlling fouling in marine environments. In recent years, non-toxic fouling resistant paints have become commercially available, several of which were selected for a freshwater field trial.

The coatings evaluated were a biodegradable wax, copper powder/polyester, polyurethane, drag reducing epoxy/polyamine, teflon and three different silicone rubbers. These were compared to uncoated controls and a standard coal-tar epoxy paint. The trial was conducted at the western forebay of Nanticoke TGS where various coated substrates, representing typical materials of construction, were immersed. Frequent inspections from March to October 1990, were completed to monitor the extent of fouling on the coatings.

By October only two paints demonstrated resistance to zebra mussel fouling. Both of these silicone based coatings showed no greater than 20% coverage by mussels and could be easily cleaned. On the other hand, all other coatings, the uncoated controls and the standard coal-tar epoxy were heavily colonized and mussels firmly attached.

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TO: Mr. M.J. Northfield
Manager
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A7 A4

EVALUATION OF COATINGS TO CONTROL
ZEBRA MUSSEL COLONIZATION - YEAR ONE
- INTERIM REPORT

1. INTRODUCTION

Since their introduction into Lake St. Clair from the ballast water of a European vessel, zebra mussels (Dreissena polymorpha) have proliferated throughout the Great Lakes during the past two years(1,2). Based on their current rate of migration, it is expected that these molluscs will infest most fresh water rivers and lakes in North America within the next few years.

It is well known that zebra mussels will adhere to and colonize any non-toxic solid surface such as steel and concrete. Consequently, enormous fouling problems have been experienced by many industries drawing raw cooling water from Lake Erie. For example, in the summer of 1989, the Detroit Edison Monroe power station was forced to temporarily shut down because of condenser tube blockage by zebra mussels. Fouling problems were also experienced by power plants in Ohio as well as Ontario Hydro's Nanticoke TGS since 1989.

At the moment, most of Ontario Hydro's stations are chlorinating intake water from early summer until late fall when veliger mussels are available in the water column. However, there are concerns regarding the environmental impact of chlorination, including the formation of trihalomethanes and the effects of residual oxidant on other aquatic life. To develop longer term alternatives to chlorination, Ontario Hydro has undertaken a major research effort to develop effective alternative mussel controls. These include various chemical and physical measures such as ozone, protective coatings, acoustics, UV and gamma irradiation, elevated pressure and temperature and mechanical filtration.

The goal of this program is to identify coatings which could be applied throughout Ontario Hydro's stations, on structures that are susceptible to zebra mussel fouling and amenable to coating, such as bar racks, travelling screens, condenser water boxes and various intake structures. The objective of this first year interim study is to screen coatings for their resistance to zebra mussel attachment. An intensive analysis of coating performance, (adhesion strength, durability, deterioration, corrosion resistance) as well as methods of application (laboratory versus field; dry versus underwater) will be undertaken before final recommendations on coatings can be made.

The introductory sections which follow include: 1) a brief overview of the fouling process, 2) a synopsis of the history of antifouling paints and 3) criteria for coating evaluation/selection.

1.1 The Fouling Process

Biofouling occurs by a succession of events in both marine and fresh water environments. Within a few hours of immersion, a layer of organic macromolecules becomes adsorbed onto solid substrates (3, 4). This conditioning film favours the subsequent colonization by microorganisms which can only effectively attach after the adsorption of an organic film. Microorganisms of increasingly complex morphology are then attracted to this surface. The stages of this adhesion process are explained in more detail elsewhere (5, 6).

The primary attachment of bacteria is followed by attachment of diatoms, fungi, microalgae and protozoa. This eventually results in a copious slime layer or biofilm which adheres to the substrate. The rate at which a stable biofilm is produced depends not only on the season, nature and composition of the substrate, but also the chemistry, temperature and velocity of the lakewater (7).

Almost immediately after the establishment of the biofilm, macrofouling will occur. Primary fouling such as hydroids and bryozoans are the first organisms to attach. This is followed by secondary foulers such as sponges and mussels.

Thus, to test the efficacy of any antifouling materials, adequate time must be given for preconditioning of the surface before final judgements are made.

1.2 Antifouling Paints - A Historical Overview

Historically, the majority of developmental work in antifouling paints has been directed towards the prevention of barnacle growth on ships. Barnacles can impede ship movement by causing an increase in both the hull roughness and overall weight. This results in additional annual expenditures of millions of dollars in fuel penalties and barnacle removal (8).

A general historical outline of the developments in antifouling coatings is given in Table 1. Clearly, the current trends are toward the use of environmentally benign coatings such as silicone rubber. The ever increasing public concern over environmental impact was a factor during the process of selecting test coatings, eg. excluded organotins.

1.3 Selection of Coatings and Test Materials

Test paints were selected by the following criteria:

1. Proven antifouling performance of the coating or similar coatings in marine environments.
2. Fouling resistance and/or an easily cleaned surface.
3. Must not release unacceptable levels of toxins such as heavy metals. This immediately precluded tin based coatings.
4. A service life of at least two years.

5. Immediate availability and

6. Can easily be applied on steel and concrete surfaces.

Based on the above criteria, antifouling coatings listed in Table 2 were chosen. Selection was based on methods of applying coatings, including underwater application. It was necessary to evaluate the selected coatings under freshwater conditions because their performance previously had been determined only under salt water conditions. The most common construction materials in use which would require protection against mussel attachment are carbon steel, stainless steel and concrete. These materials were therefore chosen as test substrates. To study the interaction of corrosion and fouling, carbon steel plates with and without cathodic protection were used.

Carbon steel (with and without cathodic protection) plates and the concrete plates were coated. These were compared to uncoated control plates and plates coated with coal-tar epoxy, which is typically used as an anticorrosion coating on submerged structures throughout Ontario Hydro. No coatings were applied to the stainless steel plates.

The western forebay of Nanticoke was chosen as the test site. This area was selected since it is readily accessible and was heavily infested with mussels in the previous year. It was expected that similar fouling would occur in 1990 and subsequent years.

2. MATERIALS AND METHODS

2.1 Initial Preparation of Steel and Concrete Plates

2.1.1 Carbon Steel

Prior to coating, a total of 80 precut carbon steel plates (6 x 8 x 1/8") were sand blasted to a white finish (SSPL-SP-5, NACE No 1). All plate edges were smoothed by sanding and the plates then weighed. Plates were then tightly wrapped in a plastic film (Saran Wrap, Union Carbide) to prevent spot rusting, stored at room temperature and unwrapped just before paint application.

For the cathodically protected (CP) plates, the anode/cathode attachments were prepared by spot welding two stainless steel wires separately to each opposite end of one of the 6" plate sides. After spot welding, the wires were insulated by the application of heat shrink sleeving and the weld connection secured with epoxy (Araldite AV-138/HV-998, Ciba-Geigy). Plates were weighed before and after wire attachment, wrapped in plastic film and unwrapped before painting.

2.1.2 Concrete

In total, 60 concrete plates (6 x 8 x 1/8") were prepared by the Concrete Technology Section (OHRD) by pouring "fast cure" concrete into preformed molds and allowing to cure for 7 days. After a further 30 days of curing, plates were cleaned of surface calcium carbonate with 10% HCl and further washed with distilled deionized water. The wet plates were allowed to dry and stored at room temperature. Prior to paint application, plates were oven dried at 50° C overnight and allowed to cool at room temperature.

2.1.3 Stainless Steel

Stainless steel plates, SS 304 and 316 (6 x 8 x 1/8"), were degreased with acetone and/or trichloroethylene prior to weighing and subsequent preparation.

Table 1 Historical Development of Antifouling Paints

Time Period	Coating(s)	Comments
ca. 500 BC to 1800's	Copper sheathing	Effective until surface oxidized. Caused corrosion of iron hulls. Copper based paints currently available for sailing craft (9).
Mid 1800's to 1920's	Shellac paints mixed with salts of mercury, tin, arsenic and lead.	Formulation based on trial and error.
1930's to WW II	Coatings based on a wider wider variety of heavy metal toxins.	Rigorous studies on the effect of toxins on fouling organisms.
WW II to mid 1950's	Major scientific effort by UK and US led to tougher binders such as epoxy and vinyl. Development of organic biocides.	Maximum of two years of effectiveness. Undesirable toxic effects on other marine life. Organotin coatings believed to be non-toxic.
1960's and 1970's	Self-polishing tin polymer coatings.	Maintained effect by continual hydrolysis of topcoat (10). Achieved up to five years service life (11, 12, 13). Mercury, arsenic and lead paints banned.
1980's		Major concerns over the accumulation of tin in marine life (14, 15). Tin paints banned.
	Use of non-toxic silicone paints.	Outstanding performance but physically weak (16-19).
	Highly loaded teflon coating	Tougher than silicones and fouling is easily cleaned (20).

Table 2 List of Coatings Evaluated

[1] Coating		Reported Mode of Action
Biodegradable Wax (WAX)		An "easy clean" (wax) coating from which fouling and coating detach together.
Polyurethane (PU)		Durable underwater paint from which fouling can be easily removed.
Ceramic filled Epoxy/Polyamine (E)		High gloss, low drag paint from which fouling can be cleaned.
Teflon (Tf)		Underwater protective coating to which fouling is weakly attached.
Copper Powder/Polyester (Cu)		Widely used as antifouling paint on sailing craft. Toxicity of copper ions on fouling is well known.
Silicone (Si)	1 2 3	Low surface energy coatings to which fouling organisms become weakly attached.

[1] To maintain confidentiality during this program, manufacturers and/or brand names are not listed.

2.2 Application of Antifouling Paints

All plates were weighed before and after paint application and coated in the same way: completely on the (upper) surface to be exposed to mussel fouling, on all edges and on the lower surface extending one inch from the plate edge. The methods by which the individual paints were applied are listed in Table 3.

2.3 Preparation of Plates Before Attachment to Panels

After identification numbers were written onto the uncoated underside of each plate, a layer of molten beeswax was applied to the entire uncoated area, including the coating/substrate boundary. This was done to prevent water ingress which would occur at the unprotected coating edge. The prepared plates were again weighed after the beeswax had hardened.

Table 3 Methods of Paint Application

[a]Coating		Application Method
Coal Tar Epoxy (CTE)		Airless Spray
Biodegradable Wax (Wax)		Brushed onto CTE coated plates
Copper powder/(Cu) polyester		Brush
Polyurethane (PU)		Brush
Teflon (Tf)		Conventional Spray
Epoxy/Polyamine (EP)		Brush
Silicone (Si)	1	Cast on
	2	[b]Airless spray
	3	[b]Airless spray

[a]Primers and paints were supplied at no cost by the manufacturers. Spray application was carried out using either a President airless or conventional sprayer (Graco, Mississauga, Ontario)

[b]Concrete and steel plates were prepared by the paint suppliers according to our specifications.

To evaluate coating deterioration after exposure, coating thicknesses were recorded before and after immersion. Paint thickness on steel plates was measured with magnetic thickness gauges (Mikrotest 0-40 or 0-200 ranges, Mikrotest Co, W. Germany). Coating thickness on concrete plates was estimated using the paint thickness to paint weight ratios calculated for the painted steel equivalents.

Weight and thickness measurements are not presented in this interim report but will be included in the final report, after test plates have been permanently removed and evaluated.

2.4 Plate Support Panels

2.4.1 Preparation of Panels and Attachment of Plates

In total, ten varnished marine plywood panels were each bolted to a mild steel frame which was coated with coal-tar epoxy (modified from Leitch (21), Figure 1). Eight of the ten panels were designated for plates coated with antifouling paints. One of the remaining two panels supported plates painted with coal-tar epoxy, while the remaining panel carried the uncoated controls. The test was designed to evaluate one type of coating on each selected substrate per panel.

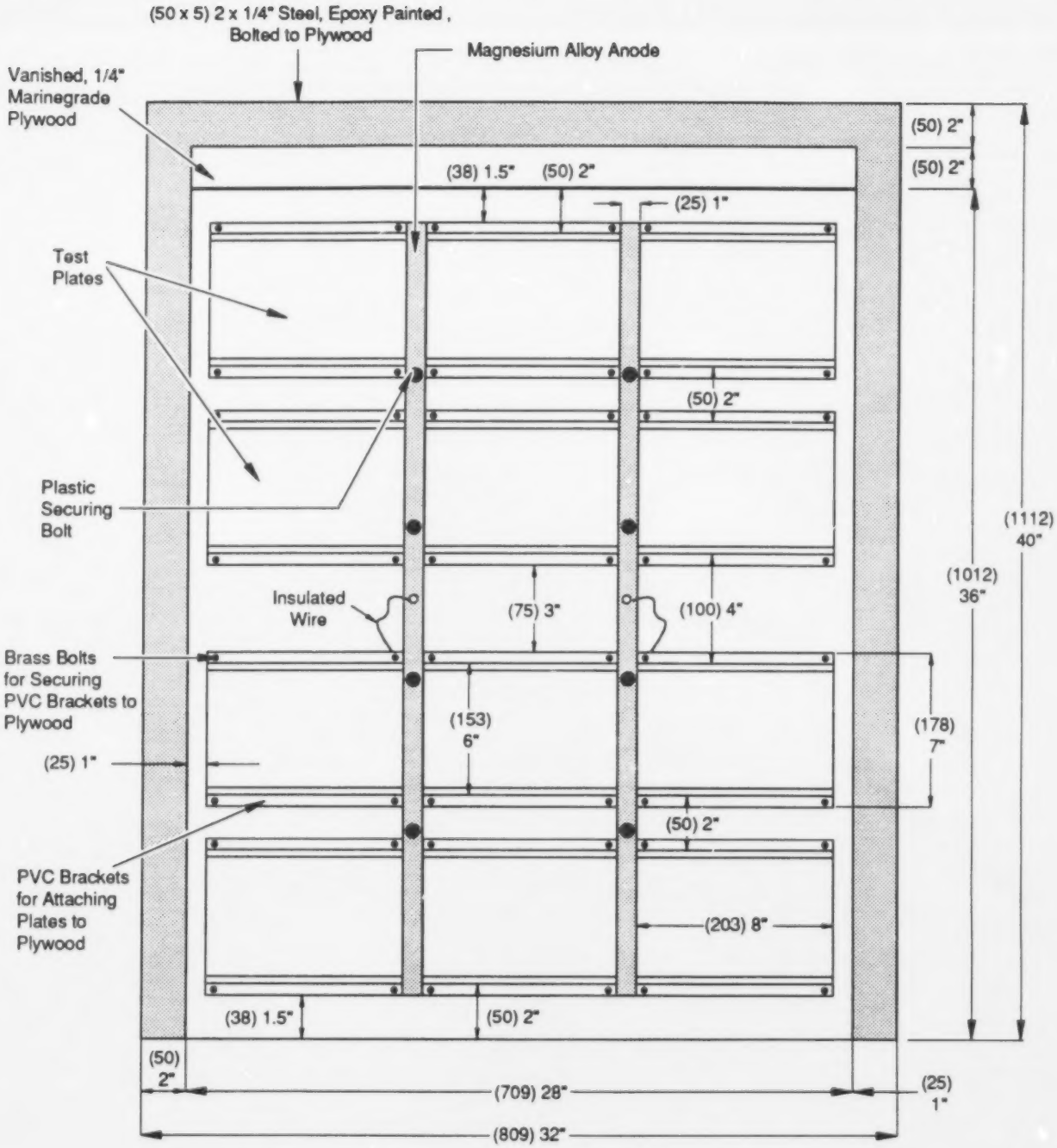


FIGURE 1

PANEL DIMENSIONS
(Inches, mm in brackets)
(Modified from Leitch (21))

The control panel as well as the panel supporting coal-tar epoxy coated plates, each held 12 plates in total: 3 carbon steel, 3 carbon steel with cathodic protection, 3 stainless steel and 3 concrete. On the other hand, each of the remaining eight panels had only 9 plates coated with a single antifouling paint: 3 carbon steel, 3 carbon steel with cathodic protection and 3 concrete.

Before attachment of the plates to the panel, a cushioning layer of 1 mm expanded neoprene rubber was inserted between the underside of each plate and the plywood frame. The plates for each panel were selected and attached in a randomized order, in a 3 x 4 or 3 x 3 array with no contact between adjacent plates. Precut PVC brackets and brass bolts were used to secure each plate onto the panel. Care was taken to avoid contact between the steel plates and the brass bolts.

Two strips of magnesium anode ribbon (36 x 3/4 x 3/8") (Corrosion Control Co. Ltd., Burlington, Ontario) were used to provide cathodic protection for selected carbon steel plates. The anode strips were positioned between plate columns 1 & 2, and 2 & 3 (see Figure 1) and fixed with nylon bolts. The wires between each cathodic plate and the anode were trimmed and the exposed ends connected to the anode using stainless steel screws. Both the nylon bolts and steel screws were epoxy coated before immersion.

2.5 Panel Immersion and Inspection

The prepared panels were transported to the selected exposure site at the western forebay at Nanticoke TGS in March 1990. Six of the ten panels (panels 1 to 6) were attached to a Dexion™ frame which was suspended by two cables and a concomitant winch/pulley system, shown in Figure 2. This ensured that during submersion, panel movement in the fluctuating currents of the forebay was restricted and uniform. During inspections, panels could be easily lifted by means of the pulley system.

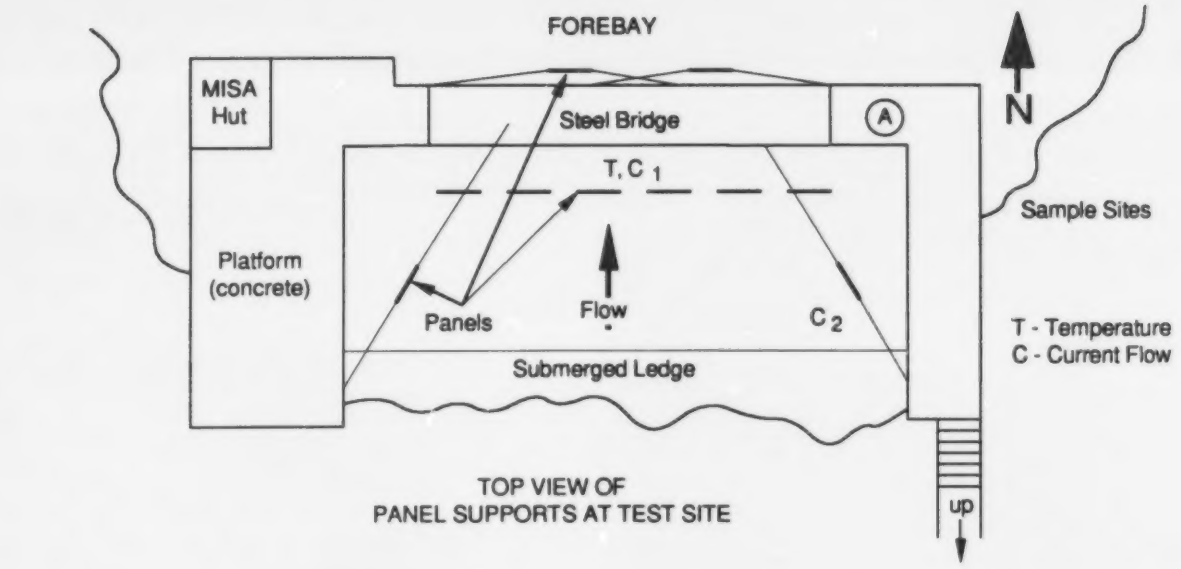
Due to space limitation in the forebay, the remaining four panels (panels 7 to 10) were supported by nylon ropes and placed in the locations shown in Figure 2. The top of each panel was immersed to a depth of 1 m ie, all plates were exposed within the upper 2 m, where zebra mussel settlement is prevalent.

After panel immersion, the following parameters were recorded: water temperature, pH, dissolved oxygen and flow rate (Hydrolab 4000, Hydrolab Corp., Austin, Texas). The level of cathodic protection was also determined (potential vs $Cu/CuSO_4$ ref.).

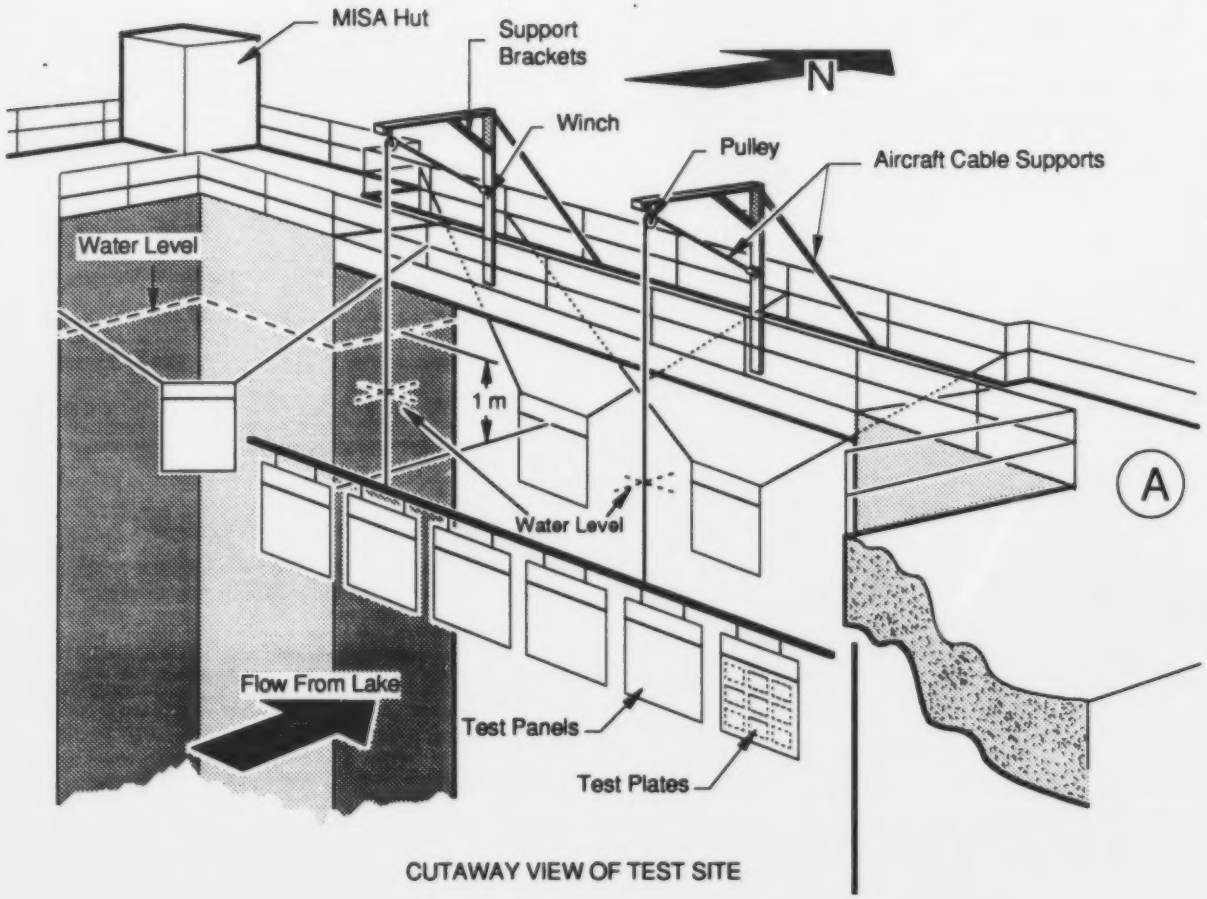
From March until October 1990, inspections of panels were performed once every three weeks. During inspections, panels were monitored for progression of fouling, signs of coating deterioration and corrosion. The panels and individual plates were photographed and resubmerged. Special care was taken to keep the panels wet while out of water.

2.6 "Finger Test" for Mussel Attachment

Upon the onset of mussel settlement, a crude on site test for strength of adhesion was applied: a finger was drawn lengthwise along the edge of a plate. Mussels which were not firmly attached were easily dislodged while firmly attached mussels remained.



TOP VIEW OF
PANEL SUPPORTS AT TEST SITE



CUTAWAY VIEW OF TEST SITE

FIGURE 2

PANEL IMMERSION SITE AT NANTICOKE TGS WESTERN FOREBAY

3. RESULTS

3.1 Forebay Conditions and Selective Plate Cleaning

For panels 1-6 and 9 and 10 which were positioned directly in the line of flow (Figure 2), flow rates varied from 7 to 12 cm/sec. On the other hand, panels 7 and 8 which were secured in the corners of the forebay experienced flow rates between 3 and 5.5 cm/sec. Water temperatures throughout the course of exposure changed from 3.8°C in March when panels were initially immersed, to 22°C in August and finally 11°C in October.

At the time panels were introduced into the forebay pH, dissolved oxygen and conductivity of the water were 7.8, 16.5 ppm and 3.1 mS/m respectively. The level of cathodic protection on uncoated carbon steel plates connected to the magnesium anode was between -1.2 to -1.3 volts (vs $Cu/CuSO_4$).

On May 15, two-thirds of all plates were cleaned of algae with a sponge brush order to avoid the possibility of the impedance of mussel attachment to the coating as a result of heavy algal coverage.

The pattern of fouling up to October 31, 1990 is described in detail in the following sections.

3.1.1 Coating Performance: March to October, 1990

Several types of primary fouling such as bryozoans, hydroids and sponges were observed on all coatings, both before and during algal and mussel attachment. The early presence of the primary fouling organisms was indicative that macrofouling was to follow. However, as coverage on all coatings was prevalently algae and mussels, the presence and number of primary fouling organisms is not reported.

To date, there appears to be no relationship between the degree of fouling and the substrate type: concrete or steel. Any differences in the levels of fouling on each panel were due to the coatings and not the substrate. Therefore, the results are discussed for each coating in general.

The plates which were selectively cleaned of algae in May, were still recognizable in June but more difficult to distinguish from uncleaned plates in July. By the start of mussel settlement in August, it was impossible to visually distinguish between plates that had been cleaned in May and those which had not. The estimated minimal and maximal percentage coverage by algae and mussels recorded on plates for each panel at every inspection, are given in Table 4.

The percent of algal fouling, mussel attachment and visible surface for the controls and coated materials vs time are shown in Figures 3A - 3J. For convenience, the worst case fouling on each panel is plotted ie, only maximum values for algal and mussel coverage and minimal values for percent visible surface are shown in these plots. No ranges for either measurements are presented.

Photographs of representative plates as they appear before immersion, on June 27 and on October 31 are shown in Figures 4A -4J (Appendix I). By October 31, mussels were approximately 1 mm in length and due to their large number, imparted a granular appearance to the photographs.

Throughout the inspections, corrosion was evident only on the uncoated and unprotected carbon steel plates (Panel 1). With the exception of Panel 5 (Sl.3) no coating showed signs of deterioration. Although a few plates on Panel 5 were accidentally scratched during handling, further deterioration or corrosion at the points

of abrasion were not evident. However, some blistering was observed on all concrete plates.

A more detailed discussion of the performance of individual coatings is given below.

Panel 1 - CONTROLS - Uncoated carbon steel (with and without cathodic protection) Concrete and SS 316 (Figure 3A, 4A and Table 4).

All substrate types showed an increasing extent of algal coverage during the period of May 15 (10-40% coverage) to June 27 (10-80% coverage. Thereafter, coverage by algae generally became less as the season continued. From August 29 until October 31, the level of visible substrate decreased due to the increase in size of mussels which initially attached in August. However, de novo mussel settlement was recorded up until at least October. The crude test for adhesion (Section 2.6) revealed that mussels were firmly attached.

Panel 2 - COAL TAR EPOXY (CTE) and SS 304 (Figure 3B, 4B and Table 4)

Algal fouling followed the same trend as seen on Panel 1. By October 31, some CTE coated plates showed slightly less coverage by mussels compared to the controls (90-95% and 100% respectively). Some areas were free of fouling and the coating was visible. Mussels appeared to adhere as firmly as for the uncoated controls.

Panel 3 - COPPER POWDER/POLYESTER (Cu) (Figure 3C, 4C and Table 4)

Up until June 27, virtually no fouling of any type was observed. Between the beginning of June to August 8, there was a slight increase in the level of algal attachment (0 to 5% respectively).

From then until August 29, there was a rapid decrease in visible coating as a result of increased algal attachment (20-87%) and mussel settlement (20-87%). This was followed by a progressive decrease of mussels to 10-60% as well as algae to 1% on October 31. Discoloration of the copper coating was eventually evident on all plates in varying degrees. This was likely the result of copper oxidation.

Panel 4 - BIODEGRADABLE WAX (WAX) (Figure 3D, 4D and Table 4)

By June 27, the amount of algal coverage had reached a maximum at 20-60%. Subsequently, coverage decreased over the following two months to 30-40%, increased in September to 20-85% and fell to a minimum level by October to 2%.

Coverage by mussels has steadily increased from August 29 (55-90%) by October 31 (85-100%). The coating was generally not visible from August 29 to October 31. Mussel adhesion was found to be similar for coal-tar epoxy.

Panel 5 - SILICONE (SI.3) (Figure 3E, 4E and Table 4)

Algal coverage, which reached a peak level by June 27 at 20-90%, was followed by a rapid decrease and plateau to 1-5% by July 18. By August 7, the attached algae were dead and decaying.

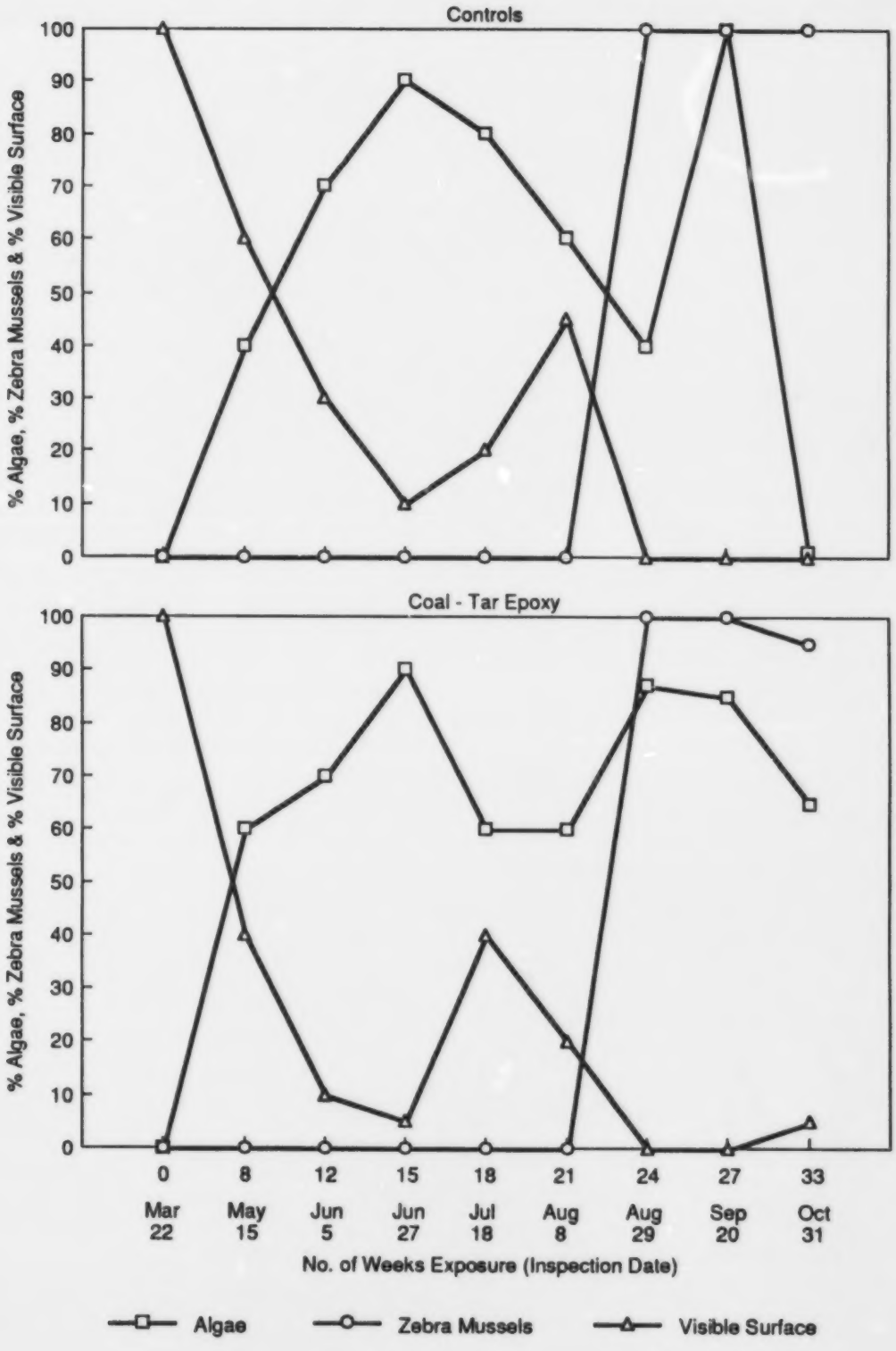


FIGURE 3A & B

% ALGAE, ZEBRA MUSSELS AND VISIBLE SURFACE VS TIME

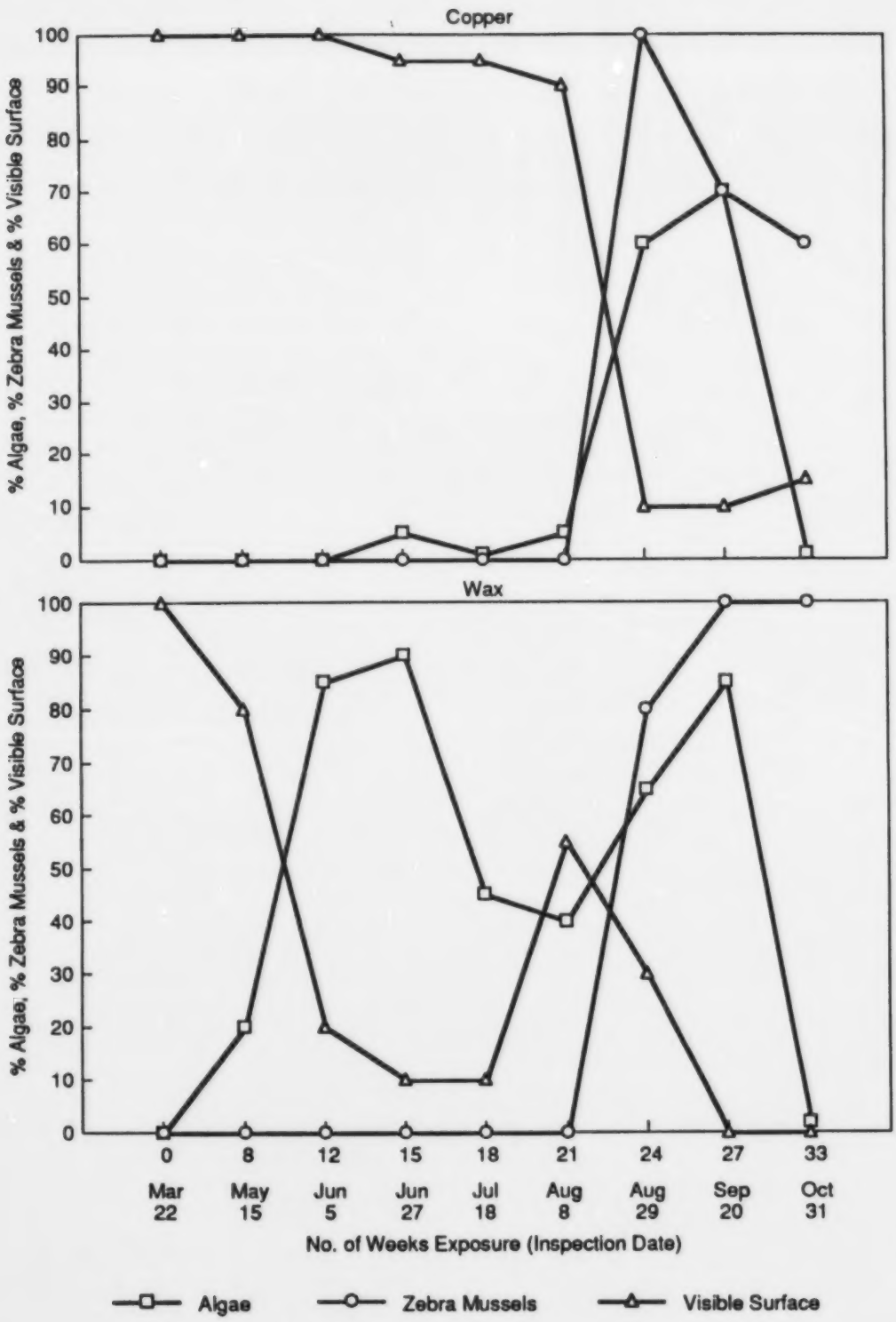


FIGURE 3C & D

% ALGAE, ZEBRA MUSSELS AND VISIBLE SURFACE VS TIME

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Mussels were observed only on the damaged areas of the paint and never exceeded 2% coverage. Both primary and secondary fouling organisms including mussels attached to the exposed undercoat. As noted earlier, paint blisters were apparent on all three concrete plates by the end of October. Slime and silt were easily dislodged with gentle finger pressure.

Panel 6 - POLYURETHANE (PU) (Figure 3F, 4F and Table 4)

Steady increases in algae were observed until June 27 when a maximum coverage of 99% was attained. Thereafter, there was a temporary drop to 10-40% per cent coverage in July followed by a steady increase to 75-95% in September before finally dropping to barely visible levels at the end of October.

Mussel coverage was consistently high at 90-100% throughout August, September and October with little variance. By August 29, there was no visible coating. Mussels were not easily removed with finger pressure.

Panel 7 - TEFLON (Tf) (Figure 3G, 4G and Table 4)

Maximum algal coverage at 55-85% was attained by June 27. This was proceeded by a significant drop to 15-20% by July 18 and an increase to 45-55% during early August. By August 29, levels again dropped significantly to 5-20% and then increased slightly by late September to 20-30%. Negligible levels were seen in late October.

Mussels were observed in high numbers (50-75% coverage) on August 29 and increased to 60-80% by September 20. By October 31, two thirds of all plates showed significant decreases in mussel coverage and resulted in an overall value 7-80%. A small amount of coating was visible by October 31. Mussels were not easily detached by the finger test.

Panel 8 - EPOXY/POLYAMINE (EP) (Figure 3H, 4H and Table 4)

A continuous increase in algal coverage from 40-50% to 75-85% was evident from May 15 until August 7 respectively. A slight decrease to 10-50% algae was noted on August 29 followed by an increase by September 20 to 50-70%. Very little algae were observed by October 31.

Mussel coverage increased from 10-65% on August 29 to 80-90% on September 20, followed by a decrease to 65-75% recorded on October 31. Between August 7 and August 27, sections of panels 1-3 were partially cleaned of fouling by accidental contact with a securing rope. However, by September 20, cleaned areas showed signs of mussel resettlement. By October 31, very little new growth on these areas was seen. Although none of the coating was visible by August 29, about 10% could be seen by September 20 and October 31. Mussels were not easily dislodged by the finger test.

Panel 9 - SILICONE (Sl.2) (Figure 3I, 4I and Table 4)

Algal fouling steadily increased up until June 27, when maximal algal coverage was observed 80-100%. A slight decrease to 60-95% was observed in July followed by a dramatic decrease 5-10% in coverage by early August. From late August onwards, virtually no algae were seen.

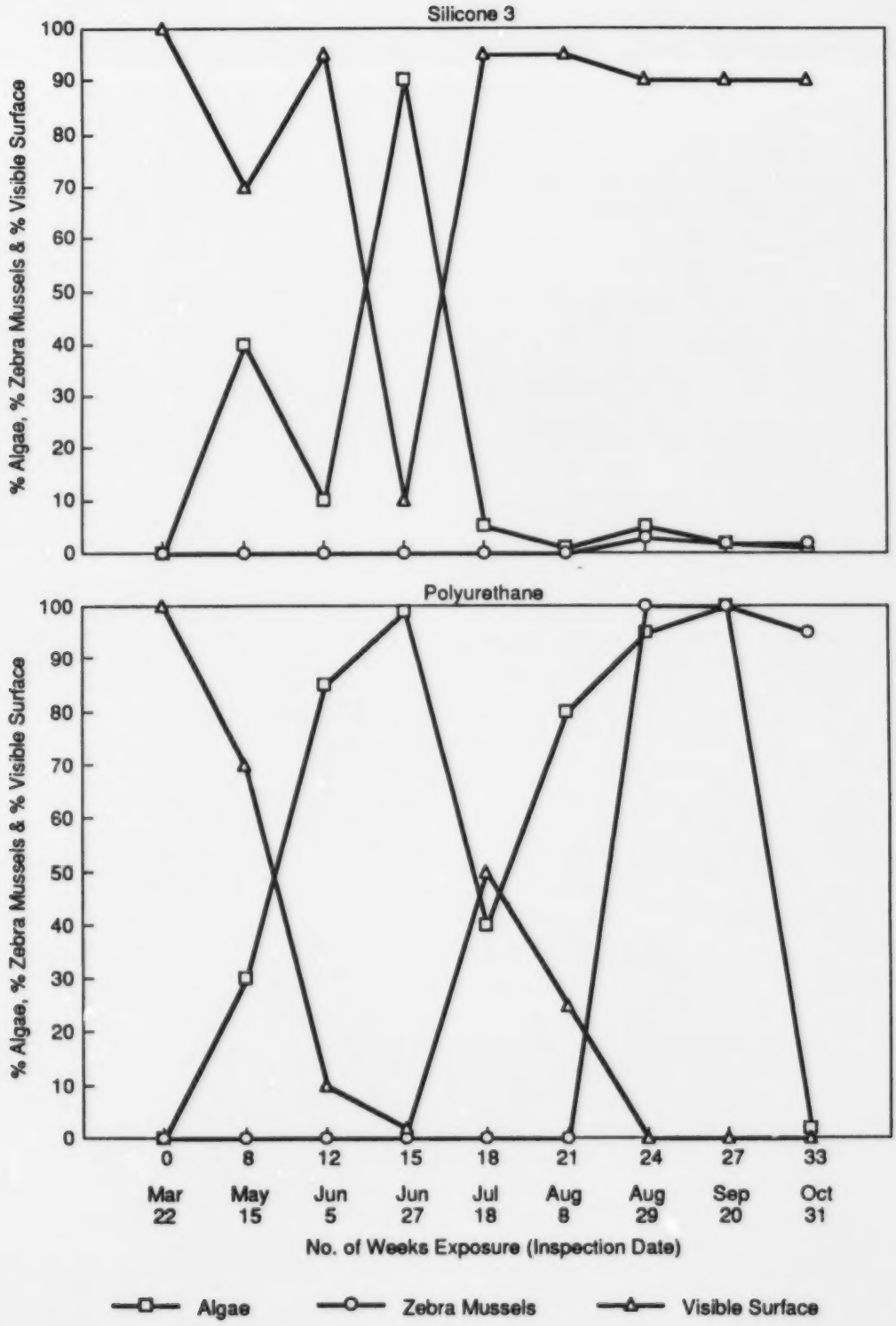


FIGURE 3E & F

% ALGAE, ZEBRA MUSSELS AND VISIBLE SURFACE VS TIME

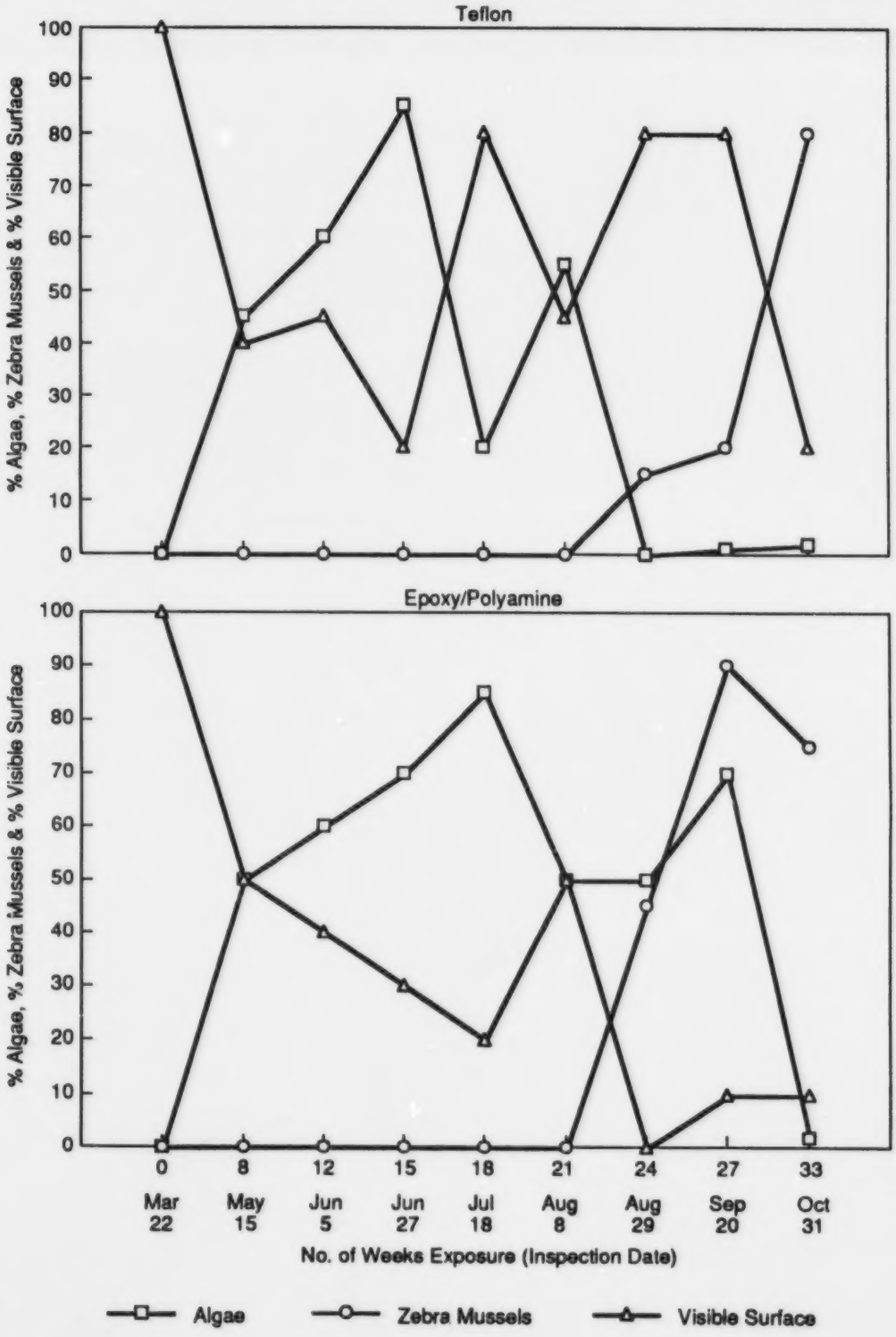
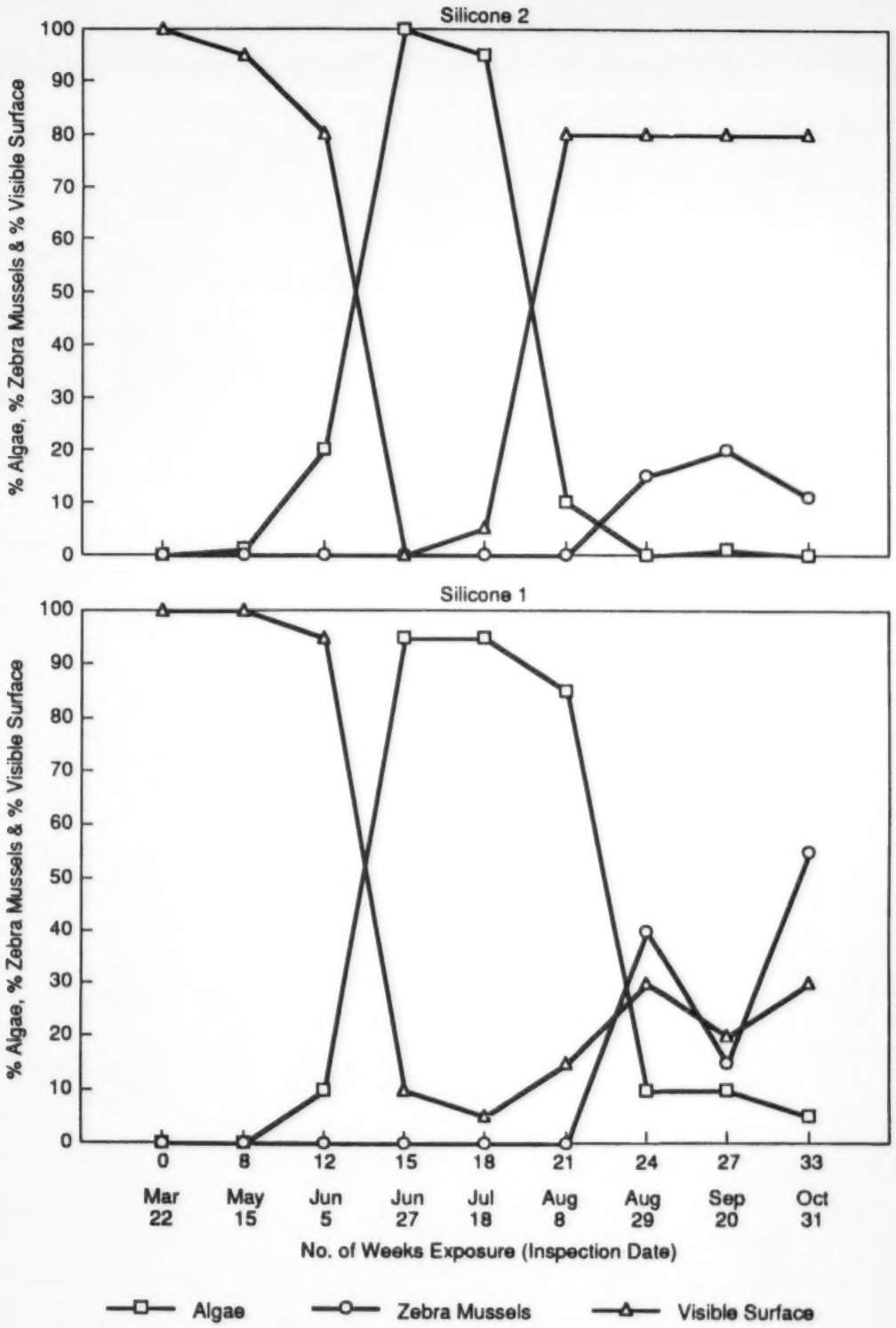


FIGURE 3G & H

% ALGAE, ZEBRA MUSSELS AND VISIBLE SURFACE VS TIME



3I

3J

FIGURE 3I & J

% ALGAE, ZEBRA MUSSELS AND VISIBLE SURFACE VS TIME

TABLE 4

Algal and Mussel Coverage for Panels 1-10

Date Water Temp (°C) Flow Rate (cm/sec) panels 1-6, 9 & 10 panels 7 & 8	Coating Panel #	Control-1	CTE-2	CU-3	WAX-4	Si 3-5	PU-6	EP-7	TF-8	Si 2-9	Si 1-10
*May 15, 1990 10.7 3 - 4 10		10-40% algae 60-90% visible substrate	40-60% algae 40-60% visible substrate	No algae 100% visible substrate	10-20% algae 80-90% visible substrate	1-40% algae 60-100% visible substrate	25-30% algae 70-80% visible substrate	40-50% algae 50% visible substrate	30-40% algae 40-60% visible substrate	1% algae 95% visible substrate	No algae 100% visible substrate
June 15, 1990 10.7 3 - 4 12		5-70% algae 30-90% visible substrate	5-70% algae 10-90% visible substrate	No algae 100% visible substrate	20-85% algae 20-95% visible substrate	5-10% algae 95-100% visible substrate	10-85% algae 10-90% visible substrate	5-60% algae 40-90% visible substrate	5-60% algae 80-90% visible substrate	15-20% algae 80% visible substrate	5-10% algae 95% visible substrate
June 27, 1990 14.5 5 - 9 2 - 4		10-80% algae 20-90% visible substrate	90% algae 5-10% visible substrate	5% algae 95% visible substrate	20-60% algae 40-80% visible substrate	20-90% algae 10-75% visible substrate	99% algae 2% visible substrate	20-60% algae 40-80% visible substrate	55-85% algae 20-50% visible substrate	80-100% algae 0-25% visible substrate	15-95% algae 20-75% visible substrate
July 18, 1990 21 5 - 9 2 - 4		50-80% algae 20-50% visible substrate	15-60% algae 40-70% visible substrate	1% algae 95% visible substrate	5-45% algae 10-50% visible substrate	1-5% algae 95-100% visible substrate	10-40% algae 50-70% visible substrate	40-70% algae 30-70% visible substrate	15-28% algae 80% visible substrate	60-95% algae 5-40% visible substrate	70-95% algae 5-25% visible substrate
August 7, 1990 21.5 n.a. 2 - 4		40-60% algae 45-50% visible substrate	15-60% algae 20-70% visible substrate	0-5% algae 90-100% visible substrate	30-40% algae 55-60% visible substrate	1% algae 95-100% visible substrate	60-80% algae 25-40% visible substrate	75-85% algae 25% visible substrate	45-55% algae 45% visible substrate	5-10% algae 80-90% visible substrate	45-85% algae 20-50% visible substrate
August 29, 1990 22 8 - 9 4 - 6		97-100% mussels 10-40% algae No visible substrate	68-100% mussels 20-87% algae 0-5% visible substrate	68-100% mussels 1-60% algae 10-25% visible substrate	55-90% mussels 15-65% algae No visible substrate	0-3% mussels (on damaged paint areas) 0-5% algae 90-100% visible substrate	95-100% mussels 75-95% algae No visible substrate	10-65% mussels 10-50% algae No visible substrate	50-75% mussels 5-20% algae 10% visible substrate	8-15% mussels No algae 80-90% visible substrate	5-40% mussels 2-10% algae 30% visible substrate
Sept 20, 1990 18.5 6 - 9 5 - 6		100% mussels 70-100% algae No visible substrate	90-100% mussels 50-65% algae No visible substrate	2-70% mussels 1-70% algae 10-15% visible substrate	67-100% mussels 20-85% algae No visible substrate	0-2% mussels (on damaged paint areas) 0-2% algae 90-100% vis.substrate (concrete blistered)	100% mussels 95-100% algae No visible substrate	80-90% mussels 50-70% algae 10-20% visible substrate	60-80% mussels 20-30% algae No visible substrate	0-20% mussels 1% algae 80-90% visible substrate	10-15% mussels 5-10% algae 20-30% visible substrate
October 31, 1990 11 11 4 - 5		100% mussels 1% algae No visible substrate	90-95% mussels 1% algae 5-10% visible substrate	10-60% mussels 1% algae 15-20% visible substrate	85-100% mussels 2% algae 0-10% visible substrate	0-2% mussels (on damaged paint areas) 1% algae 90-100% vis.substrate	90-95% mussels 1% algae 0-10% visible substrate	65-75% mussels 2% algae 10-25% visible substrate	7-80% mussels 2% algae 20-25% visible substrate	1-11% mussels No algae 80-90% visible substrate	10-55% mussels 5% algae 30-50% visible substrate

* selective plate cleaning

Some mussel attachment was evident by late August with coverage peaking at 0-20% in September. By the end of October, mussel coverage had fallen 1-11%. During the September inspection notable coverage by slime were observed. About 80% of the coating was visible by the end of October. Mussels were easily dislodged with gentle finger pressure.

Panel 10 - SILICONE (Si.3) (Figure 3J, 4J and Table 4)

The first signs of algal attachment were seen on June 5 at 5-10%. Significant increases were noted until a maximum of 78-95% was recorded on July 18. The level of coverage fell to 45-85% by early August and dramatically dropped to 2-10% during late August and September. By late October, only 5% algal coverage remained.

Mussels were first observed on August 29 at 5-40% coverage. The percentages dropped during September to 10-15% coverage then increased to their highest level of 10-55% by the end of October. Mussels were not removed by gentle finger pressure.

Based on their antifouling performance, each coating was ranked from 1 (best) to 8 (worst) as shown in Table 5. From these rankings, recommendations for each coating were suggested as outlined in Section 6.0.

4. DISCUSSION

4.1 Coating Performance

4.1.1 Uncoated Controls

The algal fouling patterns illustrated in Figure 3A, typify the seasonal events that occur in Lake Erie:

i) An initial appearance in May,

ii) Increased coverage during the summer months followed by

iii) A reduction in attached algae due to algal detachment as a result of increased growth and subsequent breakage of algal filaments,

iv) An increase due to recolonization, and finally

v) A rapid decrease in algae resulting from the onset of colder temperatures in late September and early October.

There were no visible differences in the levels of algal attachment on either the concrete or stainless/carbon steel plates. Flow rate and temperature were uniform over the panel and regardless of the material type, the surface roughness was sufficient to promote coverage by biofilm and initial settlement of algal cells. Selective plate cleaning on May 15, did not inhibit reattachment by algae and colonization by mussels.

Although, veligers were detected in the water column from June onwards by other research groups, no major post-veliger settlement on plates was observed until mid August. The degree of mussel adhesion was

Table 5

RELATIVE RATINGS OF ANTIFOULING COATINGS TESTED

COATING	+RANK	REPORTED PERFORMANCE	OBSERVED BEHAVIOUR	RECOMMENDATION
Si.3	1	Excellent resistance to marine fouling.	Outstanding resistance to mussel attachment except for damaged areas of paint. Concrete samples show blistering.	Continue trial for another season.
Si.2	2	Excellent resistance to marine fouling.	Excellent overall performance.	Continue trial for another season.
Si.1	3	Excelelnt resistance to marine fouling.	Mussel attachment and survival	Not recommended.
Cu	4	Toxic to fouling organisms.	Mussel attachment and survival.	Not recommnded.
Tf	5	"No stick" surface and readily cleaned of fouling.	Mussels attach and not easily cleaned.	Not recommended.
EP	6	Easily cleaned of fouling.	Mussels attach and not easily cleaned.	Not recommended.
WAX	7	Easily cleaned of fouling.	Mussels attach and not easily cleaned.	Not recommended.
PU	8	Easily cleaned of fouling.	Mussels attach and not easily cleaned.	Not recommended.

+RANK: 1 = BEST, 8 = WORST

sufficient to maintain 100% coverage to at least October. However, most if not all mussels are expected to detach and move to deeper and warmer waters during the winter months.

4.1.2 Coal-tar Epoxy (CTE) Standard, Wax, Polyurethane (PU) and Epoxy/Polyamine (EP)

Although the degrees of algal coverage were different, all four coatings followed algal fouling trends very similar to the uncoated controls: two distinct algal increases followed by two rapid decreases (Figures 3A, B, D, F & H). The patterns for mussel attachment were nearly identical. Neither the Wax, PU or EP coatings showed any antifouling properties compared to either the CTE standard or the uncoated controls.

4.1.3 Copper/Polyester (Cu)

Up until the 28th week of exposure, the Cu coating showed the most resistance to algal fouling of any coating tested: there was little or no sign of algal fouling (Figure 3C & 4C). This was due to the initial presence of copper ions on the surface of the coating which have a toxic effect on most fouling organisms. However, a drastic drop in performance was observed soon afterwards which can either be attributed to the oxidation of copper or an insufficient leaching rate of copper from the paint.

The rate of oxidation is dependant on water chemistry and the season. This is the main reason why there exists a controversy over the behaviour of copper as an antifouling material. Traditional antifouling paints containing copper have been reported to support the growth of algae and diatom slimes when tested in marine environments (22). It is likely that several species of freshwater algae and diatoms are also resistant to copper.

Copper ion leaching rates of 20 ug/cm^2/day are generally required to prevent settlement of diatomaceous slime (23). The leaching rates during these trials were not known.

The antifouling behaviour of the paint could be restored by abrading the surface as recommended by the manufacturer. In practice this would be a costly exercise since i) it would involve an operational shutdown and/or the services of divers to perform the actual sanding and ii) this process would have to be repeated annually to restore the effectiveness of the paint, until the topcoat eventually wears away and would require replacement.

4.1.4 Teflon (Tf)

Since its discovery, teflon has been advertised as a "non-stick" material. However, in this study, it has not shown immunity to either algal or mussel fouling. The degree of algal fouling was less when compared to the uncoated controls and the pattern was quite different (Figures 3A & G). The teflon coated materials showed fluctuations in algal coverage and unlike the uncoated controls, did not experience an increase in algae during September. This fluctuation could have been due to the more sheltered location of the teflon plates in the forebay which resulted in a greater level of slime and blue green algae. Both types of growth can impede permanent algal attachment.

Mussel fouling followed a similar trend to the uncoated controls. Mussel adhesion was such that only a few could be dislodged with gentle finger pressure. Therefore, there appears to be very little difference in the adhesion properties of teflon and the uncoated controls.

4.1.5 Silicones 1, 2 and 3 (Si.1, Si.2 and Si.3)

Algal fouling patterns for all three silicones were markedly different from the uncoated controls: a period of high or maximal secondary attachment in September, was not observed (Figures 3A, E, I and J), Si.3 showed two periods of maximum algal fouling while Si.1 and Si.2 showed one. By the 24th week of exposure, Si.3 and Si.2 showed virtually no algal fouling while Si.1 still had approximately 10% residual fouling.

Although Si.1 is the most durable of the silicones, its resistance to mussel attachment is far less than the other two. Mussel adhesion was not noticeably different than on teflon. It is well known that attempts to toughen silicone paints have always resulted in diminished antifouling performance. The development of a coating with both desirable properties remains a challenge to the paint industry.

Although both Si.3 and Si.2 have lived up to their antifouling expectations, they remain physically weak coatings which can easily be damaged and lose their antifouling properties as was the case with Si.3. Si.3 showed the most resistance to mussel attachment and mussels were only observed on areas of the coating where the topcoat was accidentally scratched during panel immersion. Si.2 was intermediate between Si.1 and Si.3 in its antifouling performance. A maximum of 20% mussel coverage was observed and mussels were never firmly attached.

4.2 Biofouling Sequence

The early immersion of the panels resulted in surface preconditioning which encouraged the formation of biofilm. This critical preliminary stage ultimately led to the firm attachment of algae and mussels on all materials except Si.3 and Si.2. Generally there were two distinct pathways observed for the coatings tested:

1) Biofilm ⟶ Temporary algal attachment ⟶ Firm mussel attachment

or

2) Biofilm ⟶ Temporary algal attachment ⟶ Weak or no mussel attachment

All paints except Si.3 and Si.2 followed sequence 1). This is not surprising since both coatings have "low energy" surfaces to which adhesive materials are weakly bonded.

Normally, when post-veligers first come into contact with a surface, they explore the surface for sites of suitable settlement. Adhesion during this stage is temporary. If the surface is acceptable for permanent attachment, byssal threads and pads are then produced which firmly attach the mussel to the substrate.

Since we did not monitor mussel settlement behaviour, it is unknown whether, post-veligers are either 1) incapable of secreting byssal attachments onto "low energy" paint surfaces or 2) they are initially attached with byssal threads but are sloughed off the paint as their weight reaches a critical density. It is also unknown whether or not older thread-drifting mussels are capable of attaching to these silicone paints.

5. SUMMARY AND CONCLUSIONS

1. Eight antifouling coatings were tested against uncoated controls and coal-tar epoxy standard.

2. Only two coatings, both silicone based, (Si.3 and Si.2), demonstrated significant antifouling behaviour after one season of exposure (Table 5). Si.3 shows more fouling resistance than Si.2. However, the observed blistering of Si.3 on concrete has already eliminated its use to protect concrete surfaces.

3. Although two silicone coatings were effective in preventing zebra mussel attachment further biological evaluation and testing of physical performance will be required before their use can be recommended.

6. YEAR TWO TEST PROGRAM: 1991

The experimental protocol for this coating evaluation program in 1991 is as follows:

1. Continue forebay exposure of all panels for 12 months ie, until March 1991.
2. Remove panels with coatings ranked 3-8 inclusive (Table 5).
3. Laboratory analysis of coating deterioration for coatings included in 2.
4. Replace failed coatings with new candidate coatings, for forebay immersion.
5. Continue exposure of Si.3 and Si.2 for a second year in the forebay.

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APPENDIX 1

Figures 4A to 4J	Progression of fouling for representative plates from before exposure until October 31.

Before Exposure

June 27

October 31

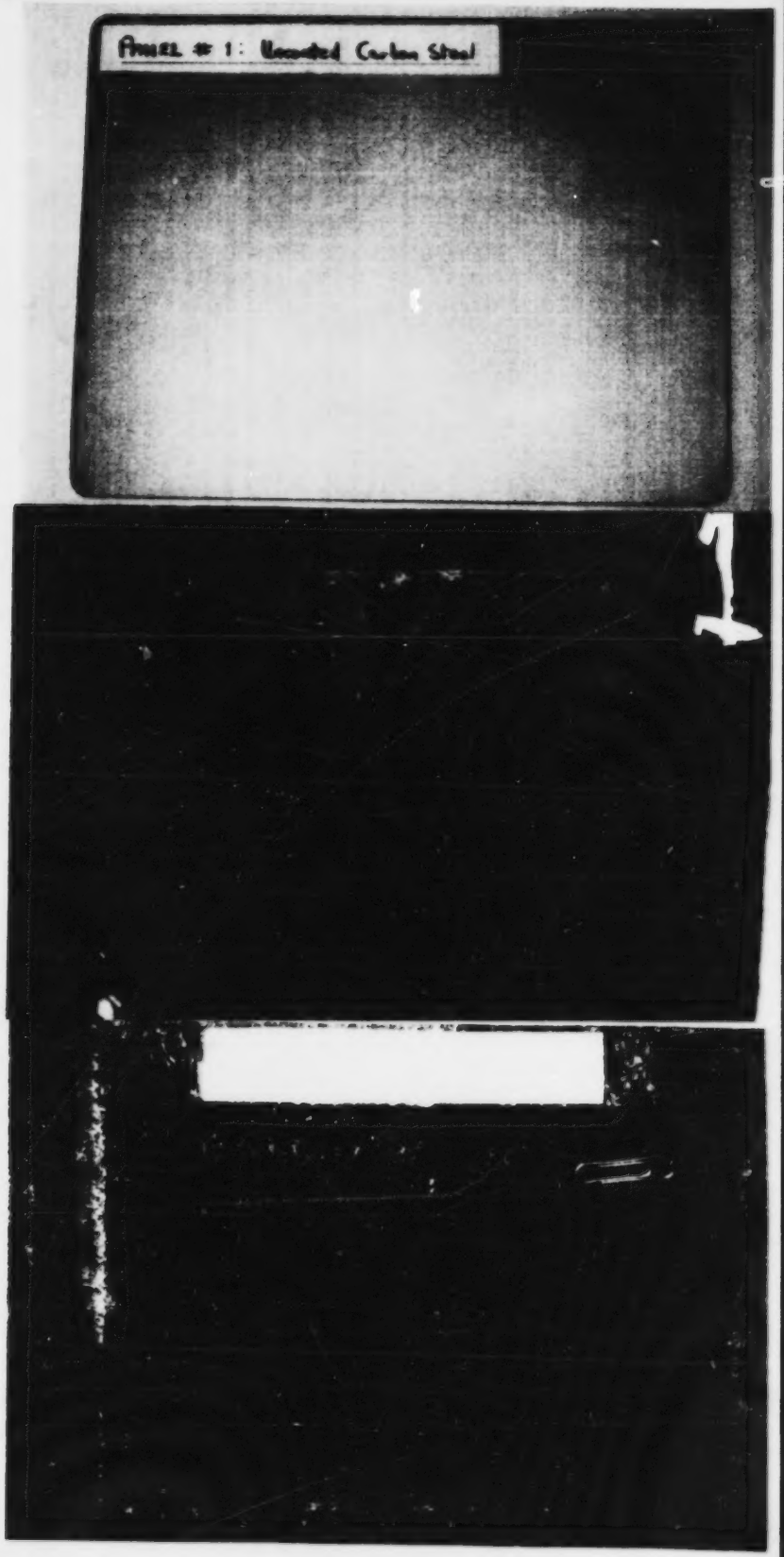
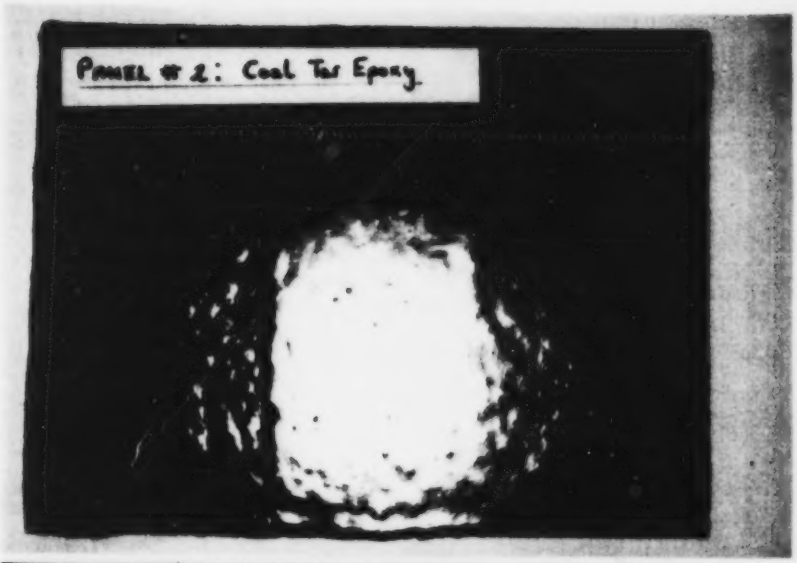


Figure 4A
Uncoated Controls

E. Leitch 1-B30

Before Exposure



June 27

October 31

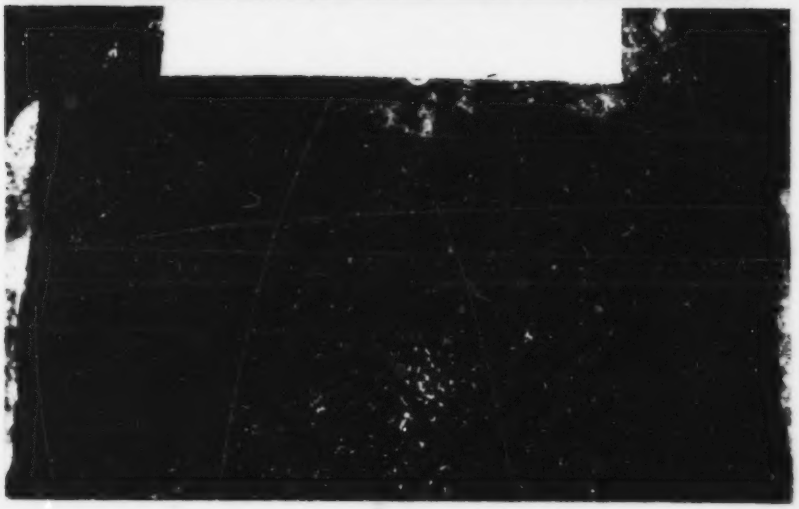


Figure 4B
Coal-tar Epoxy (CTE)

E. Leitch 2-B30

Before Exposure

June 27

October 31

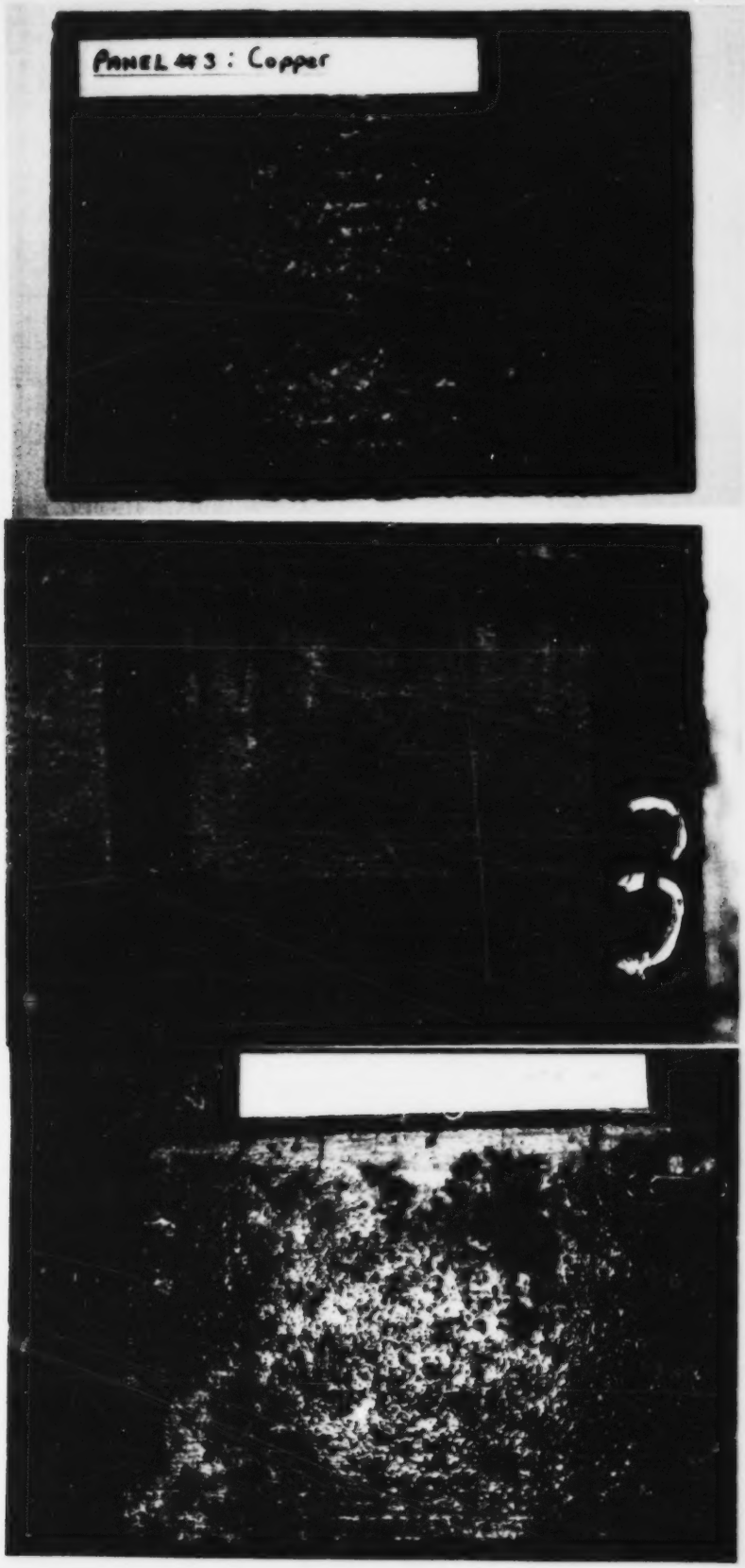
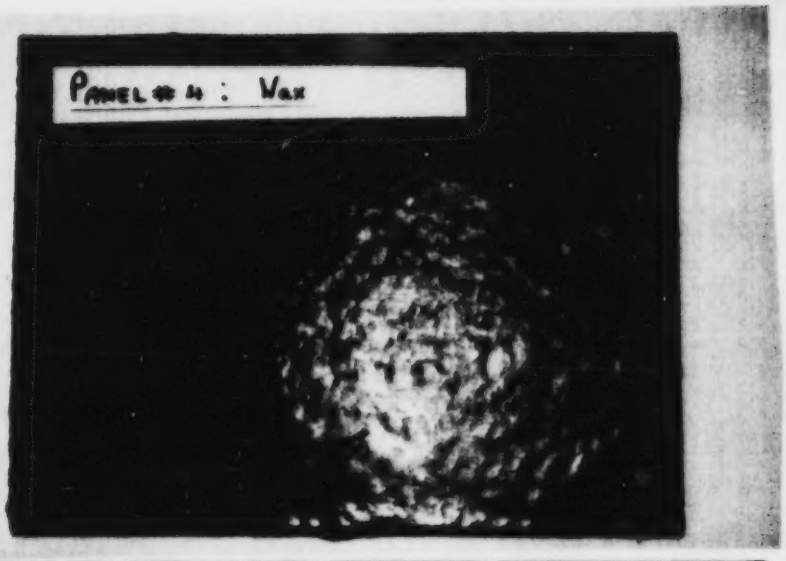


Figure 4C
Copper/Polyester

E. Leitch 3-B30

91-56

Before Exposure



June 27

October 31

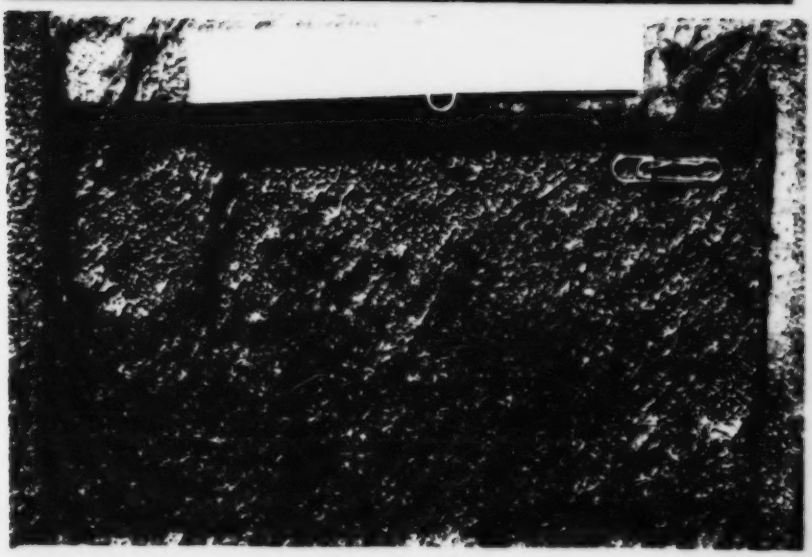


Figure 4D
Wax

Before Exposure

June 27

October 31

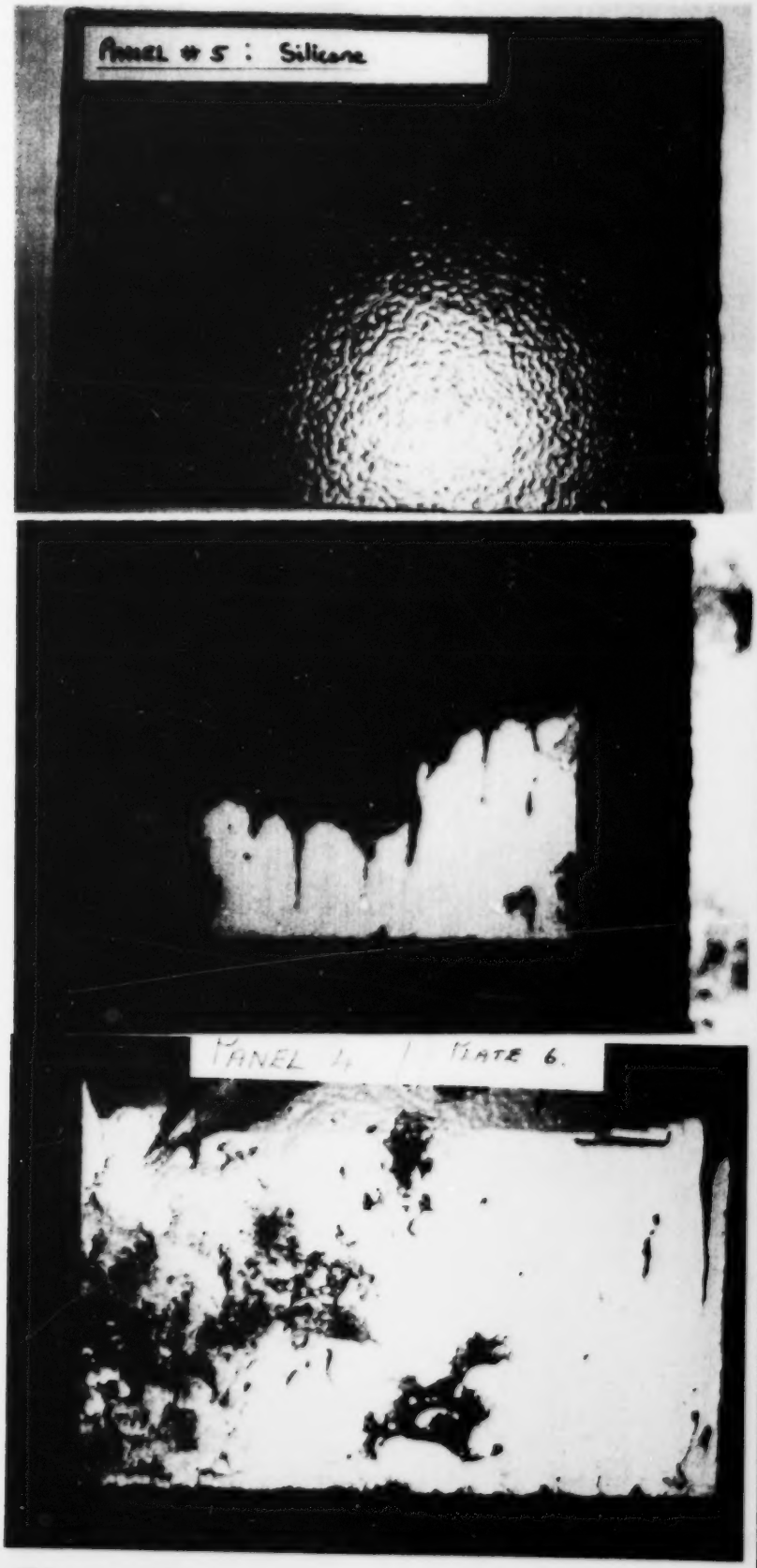
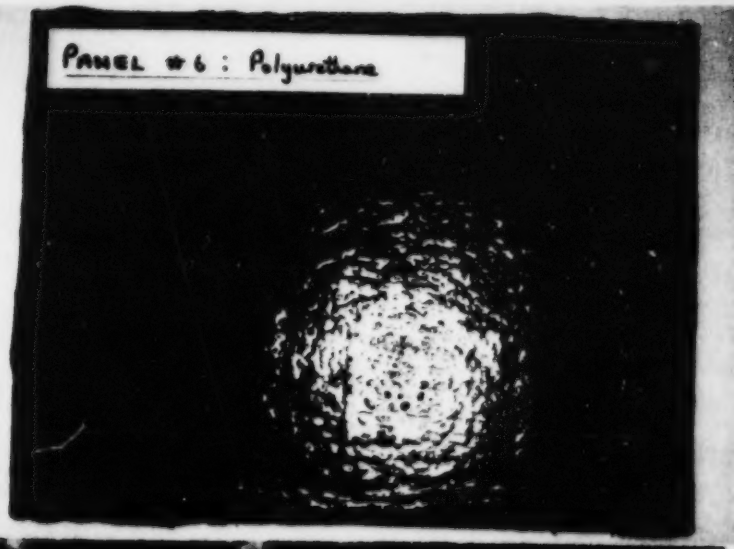


Figure 4E
Silicone 3 (Si.3)

E. Leitch 5-B30

Before Exposure



June 27

October 31

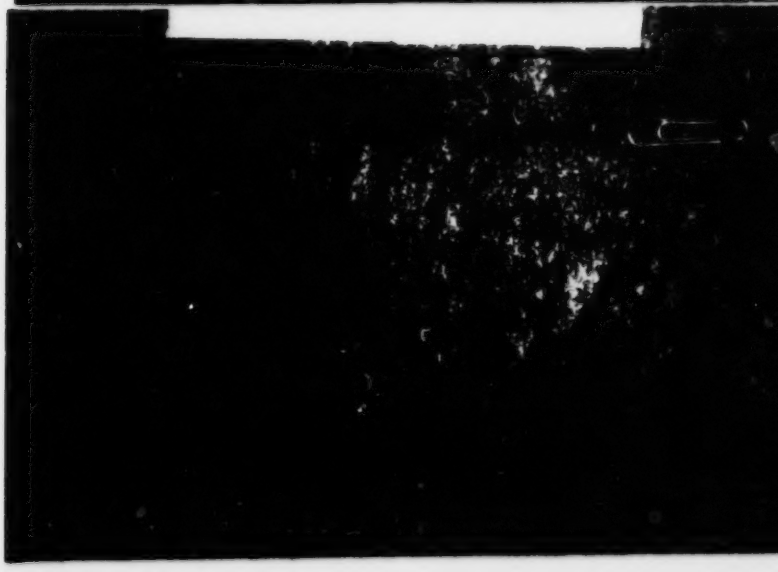


Figure 4F
Polyurethane (PU)

E. Leitch 6-B30
91-56

Before Exposure

June 27

October 31

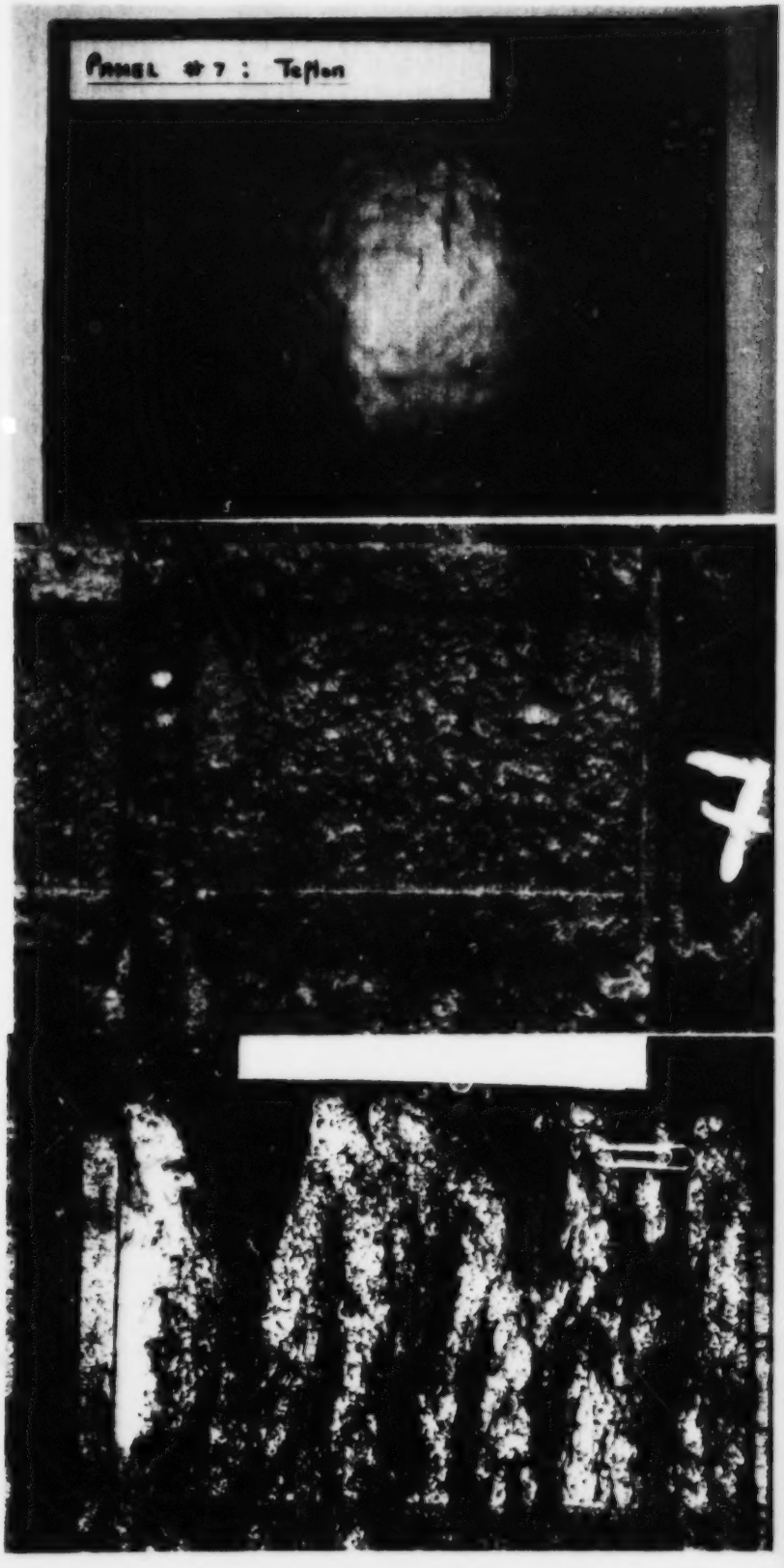
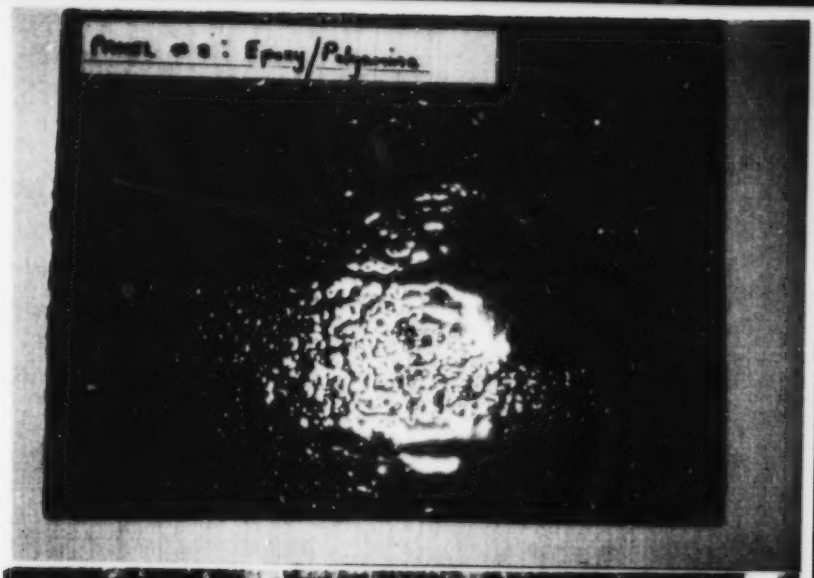


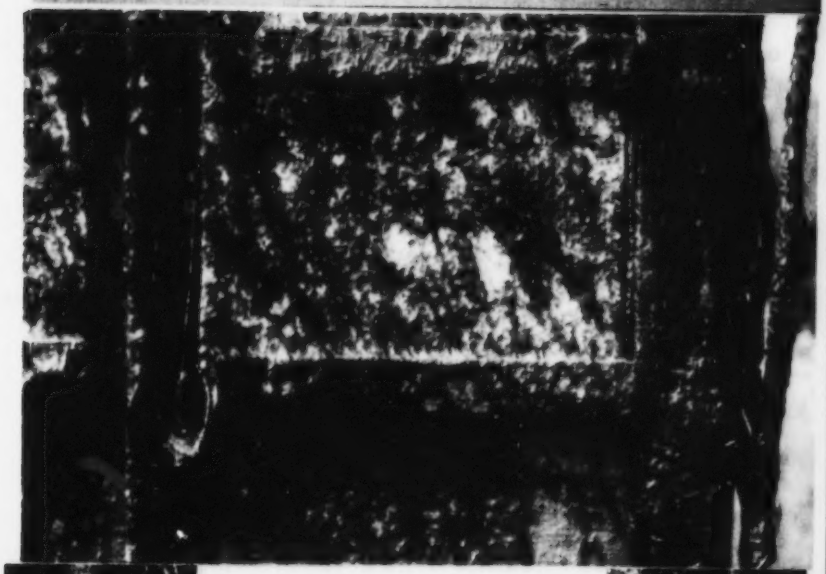
Figure 4G
Teflon (Tf)

E. Leitch 7-B30
91-56

Before Exposure



June 27



October 31

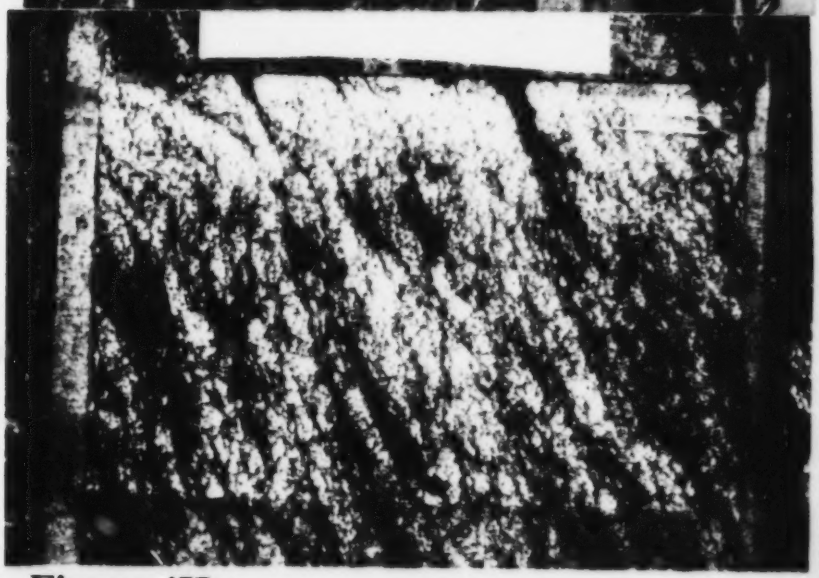


Figure 4H
Epoxy/Polyamine (EP)

E. Leitch 8-B30

91-56

Before Exposure

June 27

October 31

Figure 4I
Silicone 2 (Si.2)

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91-98

Before Exposure

June 27

October 31

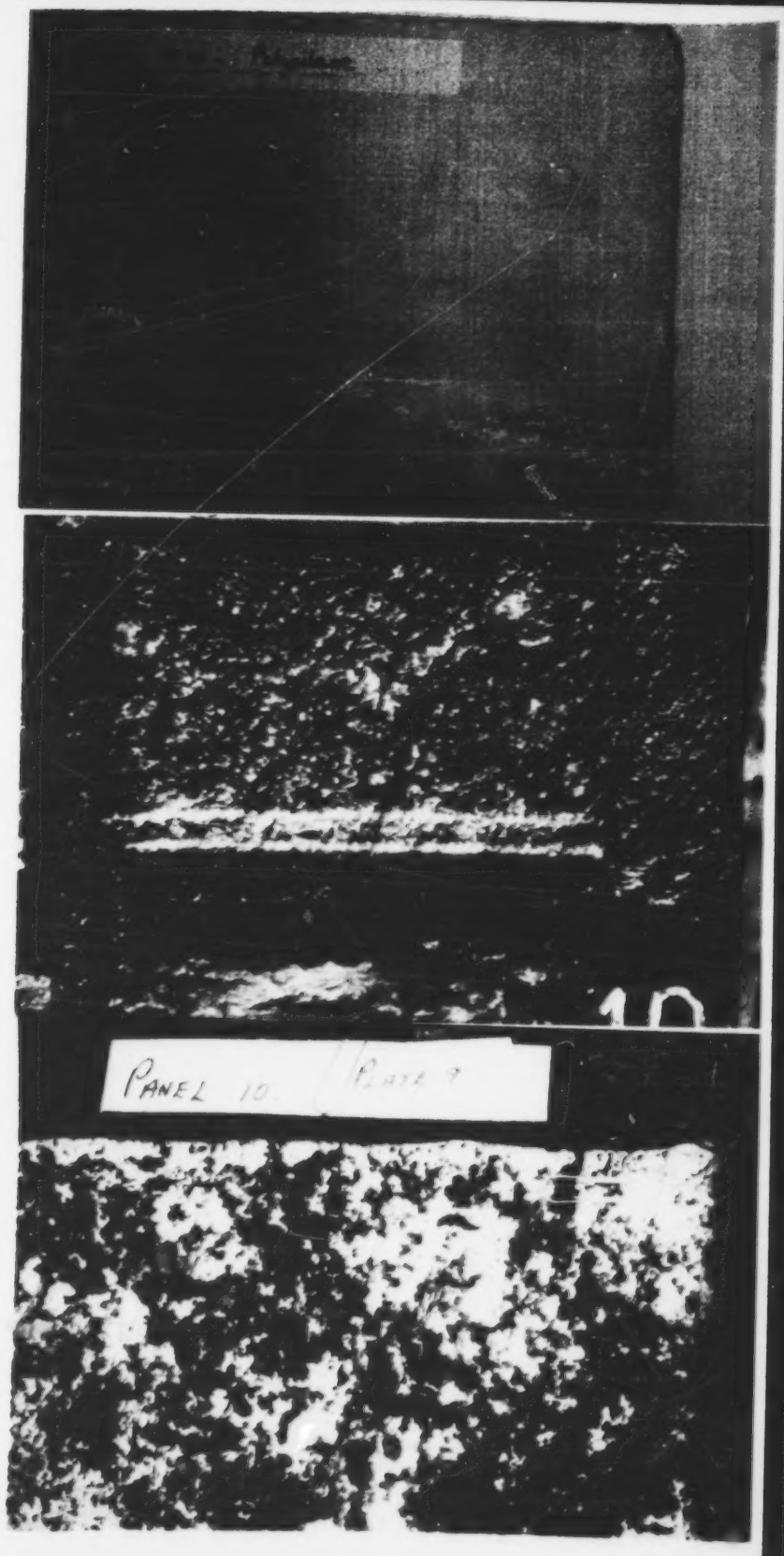

Figure 4J
Silicone 1 (Si.1)

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91-56